Supporting Information for Article

CO_2 Gasification of torrefied wood. A kinetic study.

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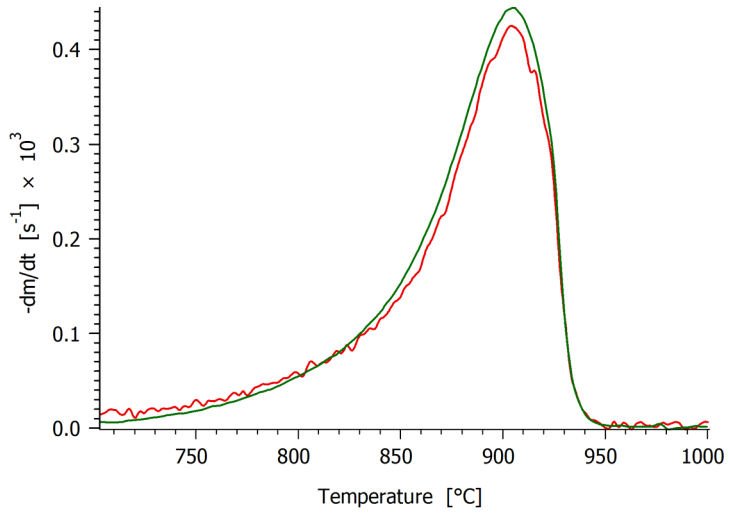
Keywords: Torrefied wood; birch; spruce; thermogravimetry; gasification; kinetics.

Scope of this document: The effect of the pyrolysis heating rate on the gasification and the repeatability of the experiments are illustrated by figures. (See the corresponding article in *Energy & Fuels* for the context.)

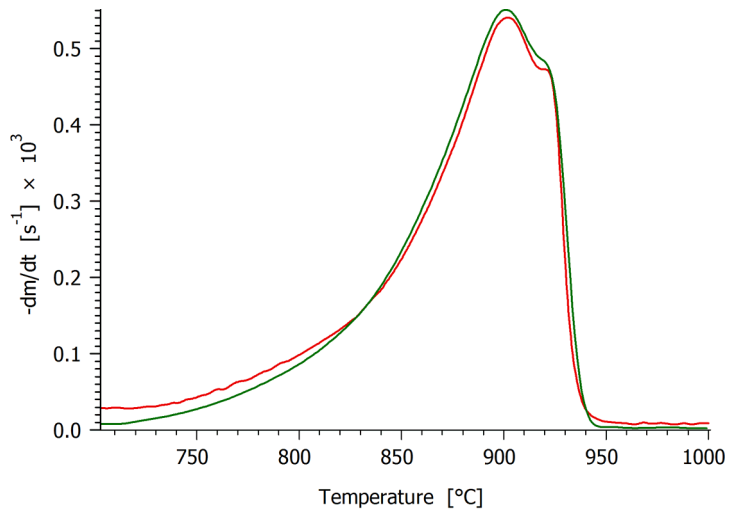
Notation in the figures: The figures display –dm/dt curves as function of temperature in the domain of gasification, where m is the sample mass normalized by the initial sample mass. Each plot contains a text field describing the experiments compared by the colors used in the plot. The description of an experiment includes the identifier of the sample, the heating program, the initial sample mass of the given TGA experiment (G_0), the date (in ISO 8601 format) when the experiment was carried out, and the height and position of the peak maximum. The peak height is expressed as percent of the initial sample mass, %/s (which is the corresponding –dm/dt value multiplied by 100).

Contents:



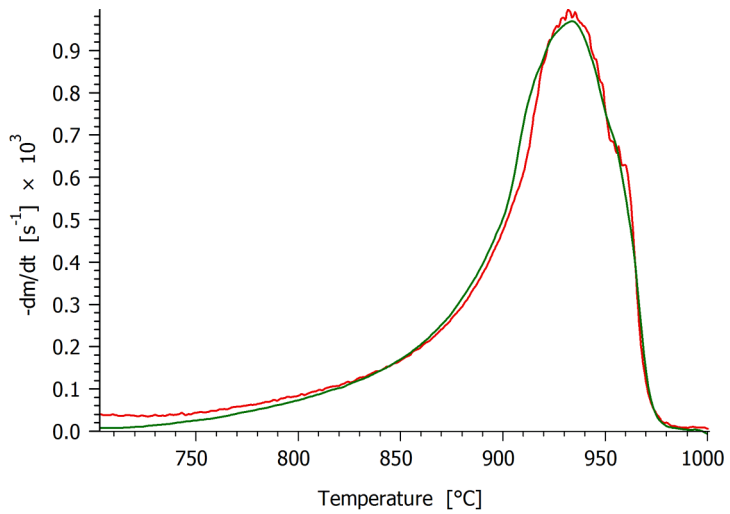
B---, 20°C/min, G_0=3.2mg, 2014-02-10
Peak maximum: 0.0425%/s at 904°C (39.28')

B---, <700°C: 2°C/min, >700°C: 20°C/min, G_0=3.2mg, 2014-04-06
Peak maximum: 0.0444%/s at 906°C (304.20')



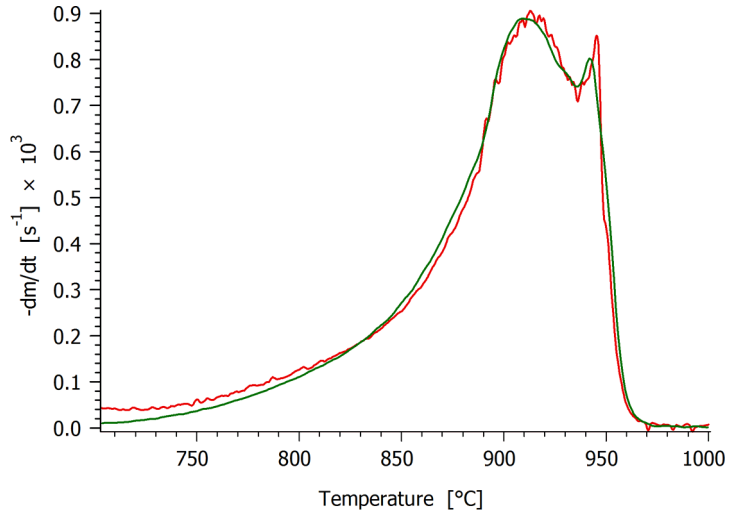
S---, 20°C/min, G_0=3.3mg, 2014-02-25
Peak maximum: 0.0541%/s at 902°C (39.18')

S---, <700°C: 2°C/min, >700°C: 20°C/min, G_0=3.3mg, 2014-04-03
Peak maximum: 0.0551%/s at 901°C (303.99')



B275, 20°C/min, G_0=2.9mg, 2014-02-24
Peak maximum: 0.0996%/s at 932°C (40.68')

B275, <700°C: 2°C/min, >700°C: 20°C/min, G_0=3.4mg, 2014-04-06
Peak maximum: 0.0969%/s at 934°C (305.63')



S275, 20°C/min, G_0=3.5mg, 2014-03-09
Peak maximum: 0.0906%/s at 913°C (39.73')

S275, <700°C: 2°C/min, >700°C: 20°C/min, G_0=3.0mg, 2014-04-06
Peak maximum: 0.0890%/s at 909°C (304.37')

Figure S1. Comparison of the gasification after heating rates of 2°C/min (dark green lines) and 20°C/min (red lines) below 700°C. The heating continued by 20°C/min above 700°C/min in both cases.

Upper row: Gasification of untreated birch and spruce wood (B--- and S---).

Lower row: Gasification of birch and spruce samples torrefied at 275°C for one hour (B275 and S275).

The lower pyrolysis heating rate resulted in lower reaction rates at the beginning of the gasification. Above ca. 820°C, however, the red and green curves are very close to each other. The closeness of the curves in this T domain reflect the repeatability of the samples, too, at low amounts of chars. For example the amount of char at 820°C were around 0.3 and 0.4 mg for samples B--- and S---. (See Table S1 below for more data.)

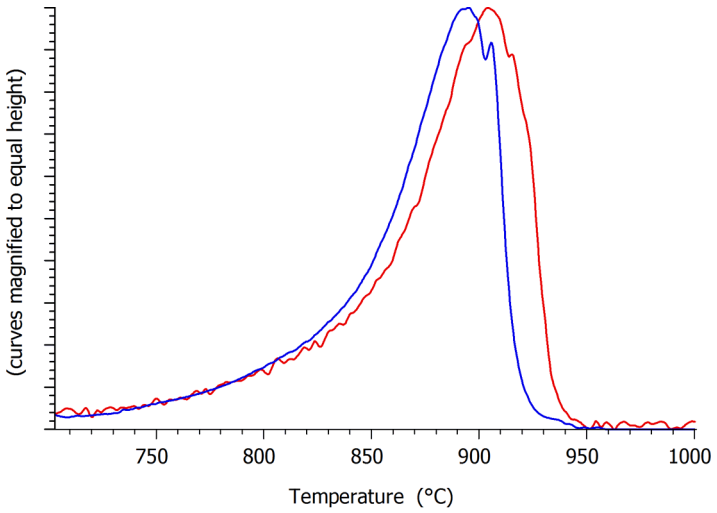
Table S1. Sample mass (G) and normalized sample mass (m) at 700 and 820°C in experiments with different pyrolysis heating rates

Sample	Pyrolysis heating rate	$m_{700°C}$	$G_{700°C}$ mg	$m_{820°C}$	$G_{820°C}$ mg
B---	2°C/min	0.09	0.30	0.08	0.27
	20°C/min	0.09	0.27	0.07	0.22
	~1400°C/min	0.06	0.20	0.05	0.16
S---	2°C/min	0.14	0.43	0.12	0.38
	20°C/min	0.12	0.37	0.10	0.30
	~1400°C/min	0.10	0.29	0.07	0.22
B275	2°C/min	0.23	0.75	0.21	0.70
	20°C/min	0.21	0.60	0.19	0.54
	~1400°C/min	0.20	0.64	0.18	0.58
S275	2°C/min	0.24	0.71	0.22	0.64
	20°C/min	0.23	0.78	0.20	0.69
	~1400°C/min	0.21	0.55	0.18	0.48

Note: It is well known that slower heating programs result in higher char yield. This knowledge is probably as old as the charcoal making itself. See the work of Antal and Grønli for more details:

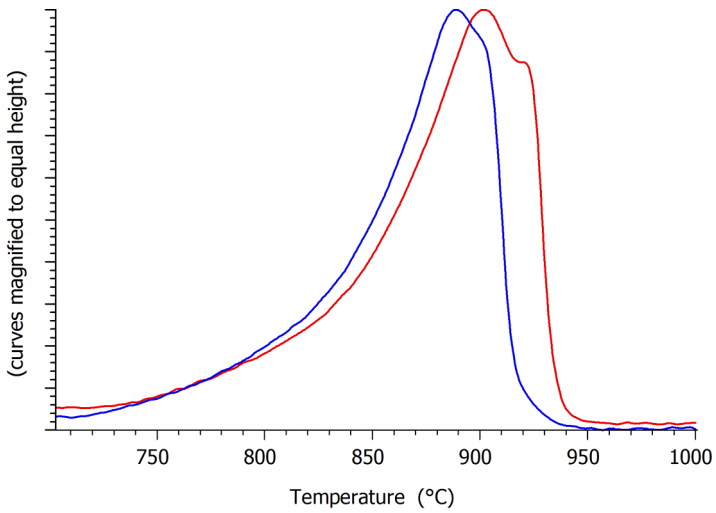
Antal, M.J.; Grønli, M. The art, science, and technology of charcoal production. *Ind. Eng. Chem. Res.* **2003**, *42*, 1619-1640.

(This rule is reflected by all items of the above table; the $m_{700°C}$ values of sample B--- are 0.094, 0.085, and 0.062 without rounding.)



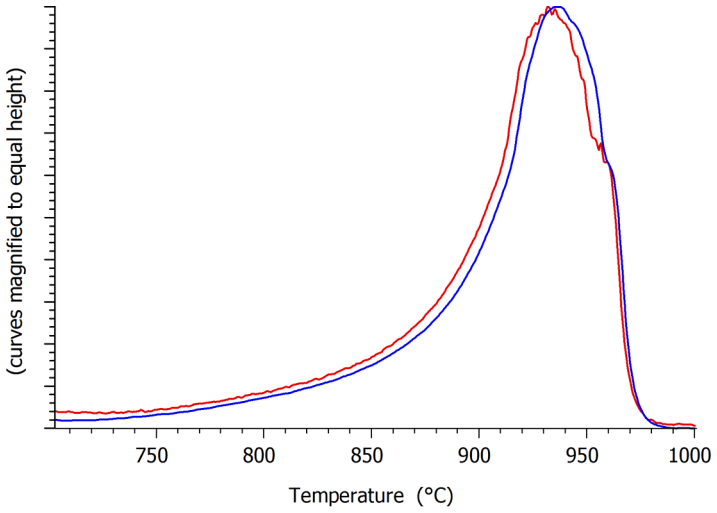
B---, 20°C/min, G_0=3.2mg, 2014-02-10
Peak maximum: 0.0425%/s at 904°C (39.28')

B---, <690°C: ~1400°C/min, >700°C: 20°C/min, G_0=3.1mg, 2014-04-02
Peak maximum: 0.0340%/s at 896°C (11.73')



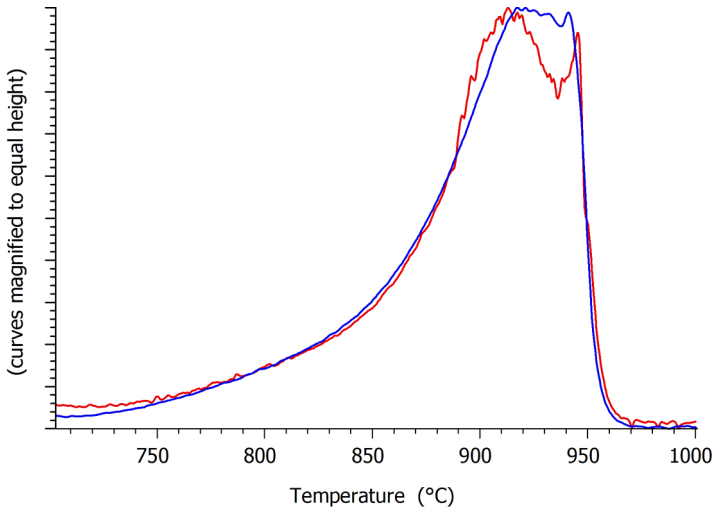
S---, 20°C/min, G_0=3.3mg, 2014-02-25
Peak maximum: 0.0541%/s at 902°C (39.18')

S---, <690°C: ~1400°C/min, >700°C: 20°C/min, G_0=3.0mg, 2014-04-02
Peak maximum: 0.0447%/s at 889°C (11.43')



B275, 20°C/min, G_0=2.9mg, 2014-02-24
Peak maximum: 0.0996%/s at 932°C (40.68')

B275, <690°C: ~1400°C/min, >700°C: 20°C/min, G_0=3.2mg 2014-04-02
Peak maximum: 0.0903%/s at 936°C (13.83')



S275, 20°C/min, G_0=3.5mg, 2014-03-09
Peak maximum: 0.0906%/s at 913°C (39.73')

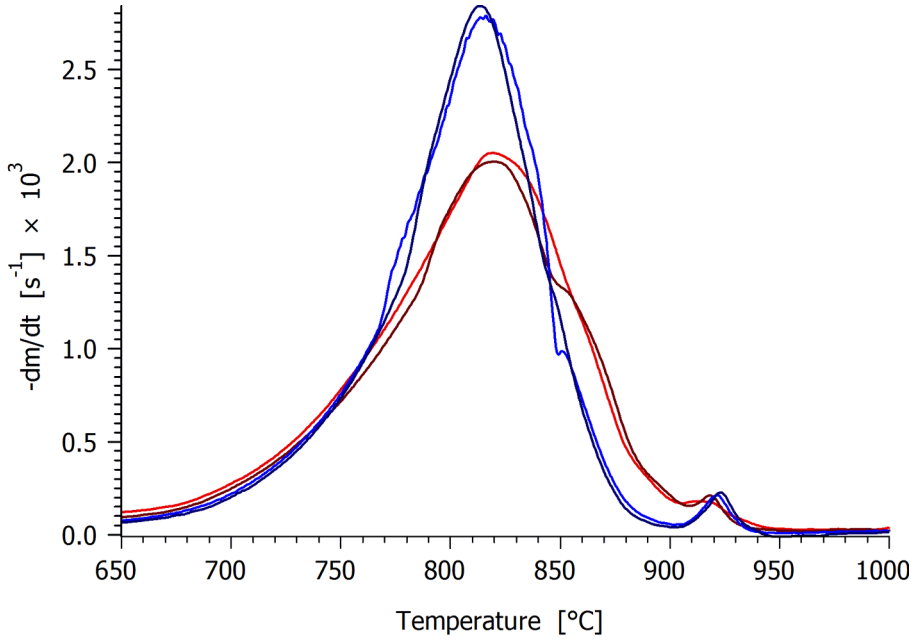
S275, <690°C: ~1400°C/min, >700°C: 20°C/min, G_0=2.6mg, 2014-04-02
Peak maximum: 0.0780%/s at 917°C (12.90')

Figure S2. Comparison of the gasification after heating rates of 20°C/min (red lines) and ca. 1400°C/min (blue lines) below 690°C. The fast heating was terminated by a short isothermal section. The heating continued by 20°C/min above 690°C/min in both cases. The curves in the plots were scaled to equal height here for a better comparison. The real heights of the curves are indicated in the text fields of the plots. Note that the fast pyrolysis resulted in less char than the slow pyrolysis, hence the heights of the blue curves are somewhat lower than that of the red curved.

Upper row: Gasification of untreated birch and spruce wood (B--- and S---).

Lower row: Gasification of birch and spruce samples torrefied at 275°C for one hour (B275 and S275).

A moderate effect was observed for the untreated woods, and a negligible effect was found for the torrefied woods.



Forest residue char 20°C/min G_0=1.0mg 2014-07-29
Peak maximum: 0.205%/s at 819°C (35.00')

Forest residue char 20°C/min G_0=1.5mg 2014-10-14
Peak maximum: 0.201%/s at 820°C (35.05')

Spruce char 20°C/min G_0=1.7mg 2014-10-15
Peak maximum: 0.279%/s at 816°C (34.85')

Spruce char 20°C/min G_0=1.3mg 2014-10-15
Peak maximum: 0.284%/s at 813°C (34.73')

Figure S3. Repeatability of char gasification experiments from a recent, unpublished work in which the experimental setup and procedure were identical to those of the present article. *Note that Figure S1 illustrates the repeatability at lower char amounts, as it was explained there.*

Notation: The red and dark red colors represent repeated gasification experiments on a char prepared from forest residue while the blue and dark blue colors belong to a spruce char.

The authors thank Mr. Tian Li for carrying out the experiments for Figure S3.